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# Biochar phosphorus (P) release is limited by high pH and excess calcium (Ca)

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## Core ideas

- P release from rice husk biochar was investigated
- Soil-free extractions were performed at different pH and solution compositions
- Lowest P release occurred at pH 7.6-8.6 and in the presence of excess Ca
- A conceptual model was developed of biochar P release in different soil conditions
- Biochars with Ca <1% and/or pH < 7.5 are optimal for maximum P release to soil

## Abstract

Aside from its use for improving soil properties, biochar is increasingly promoted as a direct nutrient provider for sustainable recycling of waste materials. However, incomplete understanding of the interacting factors that determine phosphorus (P) release from biochar may limit the efficiency of P recycling from biochar to soil. In particular, the contrasting pH of biochar and soil need to be considered. In this study, soil-free biochar (rice husk 700°C) extractions were performed under different pH (4.6–9.9) and extractant conditions to test how solution composition affects biochar P release. When solution pH was in the range 7.6–8.6 and excess Ca was present in the solution or in biochar, P release was low; only 1-7% of the total P was released compared to ~20% under most other conditions. Importantly, we demonstrate that biochar total Ca concentration is closely related to P availability ( $R^2 = 0.76$ ) and could be used to predict biochar P release. The results suggest that for maximum P release, low Ca concentrations in biochar and (soil) solution are needed and/or a pH <7.5

31 at the soil-biochar interface. This novel understanding will help engineer sustainable biochar  
32 fertilisers optimised for P provision.

33 **Keywords**

34 Rice husk; biochar pH; soil pH; calcium; slow pyrolysis

# 1 Introduction

The distinct physical, chemical and surface properties of biochar as a matrix have to be considered in understanding and assessing its nutrient value (Farrell et al., 2013; Shepherd et al., 2017; Harvey et al., 2018). The typical high porosity (e.g. 62.5-85.1% (Gray et al., 2014)) and high pH of biochar (e.g. pH 7 – 11 (Qambrani et al., 2017)) means that extraction methods optimised for soil are not necessarily appropriate for biochar. For example, in Shepherd et al. nutrients were extracted using different chemical extractants and the results were correlated with plant nutrient uptake from biochar (Shepherd et al., 2017). For phosphorus (P) it was concluded that buffered 0.01 M CaCl<sub>2</sub> correlated best with plant uptake, rather than Mehlich-3 and 2% formic acid which are typically used to determine the P availability in soil.

A factor not sufficiently quantified for biochar-containing soil systems is the influence of pH and elemental composition of the soil solution, particularly Ca for its importance in modifying P availability (Blume et al., 2016; Sun et al., 2018). The relevance of pH in explaining the effects of biochar addition to soil are evident from meta-analysis (Biederman and Harpole, 2013), but the local effects at the interface of biochar and soil require examination. When predicting nutrient availability in biochar, it is essential to consider the distinct difference in pH between biochar and soil. A pH gradient between biochar and soil will form, which could affect the release of nutrients from biochar, in particular P (Buss et al., 2018).

Hardwood and rice husk biochar released P readily and over several extraction steps when extracted with deionised water (Angst and Sohi, 2013; Qian et al., 2013). However, it remains uncertain how the interactive effect of soil solution composition and pH affects P release from biochar. Furthermore, the % P extracted from different biochars varies significantly and is strongly dependent on the type of feedstock used for pyrolysis (Buss et al., 2016a; Shepherd et al., 2017). So far it is unclear which biochar characteristics influence the P release.

Our broader aim is to optimise the composition of biochar for managing nutrients in P-constrained soils. To explore the P release from biochar, we applied conventional extractions under controlled and

uncontrolled pH conditions, mimicking different pHs and soil solution compositions at the soil-biochar interface.

## **2 Materials and methods**

### **2.1 Biochar**

Standard biochar material manufactured from rice husk was used (UKBRC, University of Edinburgh) (Mašek et al., 2018). The rice husk was sourced from Sri Lanka and produced using the UKBRC Stage III Slow Pyrolysis Unit (rotary kiln pyrolyser), described in Buss and Mašek (2014), at a highest treatment temperature of 700°C and a residence time in the heated zone of 20 min. Characteristics of the biochar (referred to as RH 700) are given in Mašek (2014). The total nutrients concentrations are (% dry basis):  $1.6 \pm 0.4$  g kg<sup>-1</sup> P,  $1.7 \pm 0.58$  g kg<sup>-1</sup> Ca,  $1.1 \pm 0.2$  g kg<sup>-1</sup> Mg,  $6.2 \pm 0.2$  g kg<sup>-1</sup> K. Further key characteristics of the biochar are as follows: ash content  $47.9 \pm 5.4$  wt%, electrical conductivity (EC)  $690 \pm 260$  µS cm<sup>-1</sup> and pH  $9.81 \pm 0.64$  (1:20 mass: volume in deionised water (DI)).

### **2.2 Rice husk biochar P extractions at different pH and soil solution composition**

Soil-free batch extractions were conducted to minimise other influencing factors in order to clearly identify the pH and solution composition effects. Different extractants were used to infer effects of soil solution chemistry on P release. The extractants used were deionised (DI) water, 0.01 M CaCl<sub>2</sub> and 1 M NH<sub>4</sub>NO<sub>3</sub>, each widely applied for soil analysis and also tested on a range of biochar materials (Angst and Sohi, 2013; Farrell et al., 2013; Zhang et al., 2016; Shepherd et al., 2017). Specifically, NH<sub>4</sub>NO<sub>3</sub> was used because it is a salt extraction similar to CaCl<sub>2</sub> but without ions that could bind to and precipitate phosphate.

A fractional factorial experimental design was implemented in which all three extractants were tested without buffering where the mean solution pHs (of the four replicates) after extraction of the biochar sample were 6.7 (NH<sub>4</sub>NO<sub>3</sub>), 8.5 (CaCl<sub>2</sub>) and 9.9 (DI). Further extractions conducted were CaCl<sub>2</sub> and

NH<sub>4</sub>NO<sub>3</sub> both buffered at pH 4.6 and 7.6 and CaCl<sub>2</sub> and DI both buffered at pH 8.6. All extractions were single step.

Buffering was implemented by the addition of the non-complexing ‘Better Buffers’ DEPP (N,N’-diethylpiperazine) at pHs 4.6 and 8.6 (pKa 4.67 and 8.83) (Yu et al., 1997) and MOPS (3-(N-morpholino) ethanesulfonic acid) at pH 7.6 (pKa 7.42) (Sari and Covington, 2005) to ensure no interaction with sorption and desorption of P. Further details of both MOPS and DEPP and their use in similar batch experiments has previously been reported (Shepherd et al., 2016, 2017). Based on this prior work MOPS was used at a concentration of 0.01 M to buffer the extraction of rice husk biochar using 0.01 M CaCl<sub>2</sub> and DI water. From our assessment of DEPP in a similar manner (Supplemental Table 1), a DEPP buffer concentration of 0.04 M was adopted.

The design outlined above provided a total of nine buffered and unbuffered extractions in the pH range of 4.6 to 9.9 (summarised in Table 1), each replicated four times. The extractions were conducted with 20 mL of solution and 0.2 g biochar (particle size 1.0–2.0 mm, representing fresh, non-weathered biochar) in 50 mL polypropylene centrifuge tubes with appropriate blanks containing no biochar (9 different blanks were used with respective extractant and with/without respective buffer). The tubes were shaken for 2 h at 150 rpm on an orbital shaker, centrifuged for 30 min at 3500 rpm and the supernatant was transferred into biotite vials using 3 mL Pasteur pipettes. The pH of the extracts at the start and end of the extraction process were measured using a Mettler Toledo FE 30 pH meter and probe calibrated with standards of pH 4.00 and 7.00 and corrected for temperature.

Table 1: Summary of the 9 extractions conducted showing concentrations of extractant and buffer (where used) and mean pH of 4 replicates after extraction of biochar sample.

Extractant and concentration	Buffer and concentration	Mean pH after extraction
0.01 M CaCl <sub>2</sub>	0.04 M DEPP	4.6
0.01 M CaCl <sub>2</sub>	0.01 M MOPS	7.6
0.01 M CaCl <sub>2</sub>	Unbuffered	8.5
0.01 M CaCl <sub>2</sub>	0.04 M DEPP	8.6
1 M NH <sub>4</sub> NO <sub>3</sub>	0.04 M DEPP	4.6
1 M NH <sub>4</sub> NO <sub>3</sub>	Unbuffered	6.7
1 M NH <sub>4</sub> NO <sub>3</sub>	0.01 M MOPS	7.6
Deionised water (DI)	0.04 M DEPP	8.6
Deionised water (DI)	Unbuffered	9.9

## **2.3 P analysis of rice husk biochar extracts**

The extracts were filtered with 0.45  $\mu\text{m}$  syringe filters (X50 Millex, MCE sterile 33 mm, Millipore, Watford, UK) and analysed for total P via inductively coupled plasma–optical emission spectrometry as described in Buss et al. (2016a). In brief, five standards of 0.01, 0.1, 1, 10 and 100 ppm P and a calibration blank were used to calibrate a Perkin Elmer Optima 5300DV. Subsequently, the extracts were analysed, and a 1 ppm standard was analysed every 10 samples for quality control to monitor any concentration shifts. Extraction blanks were measured and their concentrations subtracted from the sample concentrations.

## **2.4 Repeated rice husk biochar extraction with deionised water**

To assess the time-dependent release of P from the rice husk biochar, the RH 700 material was reduced to smaller minimum dimension (0.5 - 1 mm) using a sieve and extracted using unbuffered DI water. This reflects biochar that has been physically fragmented through exposure to physical, biological and chemical processes (Liu et al., 2017). A non-ionic surfactant, 2-octanol (98% for synthesis; Merck, Hohenbrunn, Germany) was included, to address any short-term effects of hydrophobicity that rapidly diminish in soil, and consequently to reflect long-term P leaching conditions (Ojeda et al., 2015).

Five g of RH 700 were weighed into glass bottles (Pyrex, polypropylene pour ring), and 100 mL DI water and 0.05 mL 2-octanol (solubility 1.1 g L<sup>-1</sup>; 2-octanol-biochar weight ratio 0.04:100) surfactant were added. The experiment was performed in triplicate, with the bottles shaken on an orbital shaker at 150 rpm for 1.5 h.

The mixture was filtered with Whatman No.1 filter paper and the extracts analysed for pH (as in section 2.2), electrical conductivity (EC) (Hach HQ40d portable meter, conductivity probe CDC 401) and P (see section 2.3). The filter with retained biochar was dried in an oven overnight at 80°C. The water-extraction extraction was repeated with the dried biochar and appropriate adjustment of DI water and surfactant volume to maintain the same biochar mass-to-solution volume ratio. Overall, the

extraction procedure was performed 6 times with assessment of the parameters after the 1<sup>st</sup>, 2<sup>nd</sup> and 6<sup>th</sup> extraction step.

## 2.5 Ammonium nitrate extractions of ten biochars

Calcium (Ca) is a key element that determines the availability of P in soil at elevated pHs. Therefore, 1 M NH<sub>4</sub>NO<sub>3</sub>-extractable P concentrations and total Ca concentration were determined in 10 different biochars produced at 550°C to investigate the relationship between the parameters. Details of the biochars, analytical procedures and the results have previously been reported (Buss et al., 2016a; b). The following feedstocks were used: demolition wood (DW), *Arundo donax* (ADX), sugarcane bagasse (SBI), water hyacinth (WHI), wheat straw (WSI), willow logs (WLB), winter rye straw (WRB), *Salix purpurea* (SLP), *Paulonia tomentosa* (PAT) and residues from anaerobically digested food waste (FWD).

## 2.6 Data analysis

A Shapiro-Wilk test of the P concentrations showed that the data (experiment section 2.2) were non-normally distributed. However, since one-way ANOVAs are robust against violation of the normality assumption (Schmider et al., 2010) they were conducted followed by Tukey post-hoc tests.

An exponential curve of type  $f = a * e^{-b*x}$  was fitted to previously published data for total Ca concentrations in 550°C biochars (Buss et al., 2016b) and % P availability based on NH<sub>4</sub>NO<sub>3</sub> extractions (Buss et al., 2016a) using the least-square method. All statistical analyses were conducted using SigmaPlot 13 (Systat Software Inc., Chicago, IL) and a significance level of  $p < 0.05$ .



## 3 Results and Discussion

### 3.1 Effect of pH on biochar P release

In four of the nine extractions in the pH range 4.6 - 9.9 a similar proportion (~20%; not statistically different) of the total P was extracted from the RH 700 biochar, independent of extractant and pH (extractions indicated by “a” and “ab” in Figure 1). This is noteworthy since P becomes less available in soils below pH 6.0 and between 7.5 and 9.0 (e.g. Ruyschaert et al. 2016) with the optimal P availability at pH 6.0 - 6.5 (Blume et al., 2016). Below this range, P tends to bind to aluminum (Al) and iron (Fe), while at higher pH it binds to Ca and Mg (Blume et al., 2016).

Our results suggest that inherent biochar P is released in equal amounts at pH 4.6, 6.7 and 8.6 in a soil-free system. It is expected that the soil water environment (pH, cation composition and concentration) will govern whether biochar-derived P can be utilised by plants, is leached or is immobilised, e.g. Fe and Al will partially immobilise P at a pH of 4.6 (Blume et al., 2016). At an extreme pH of 9.9, P availability assessed by DI water was significantly decreased to 12.5%, compared to the DI extraction at lower pH (Figure 1). Furthermore, the  $\text{NH}_4\text{NO}_3$ -extractable P was significantly lower at a pH of 7.6 compared to lower pHs which can be explained by P precipitation as struvite (Doyle and Parsons, 2002).

Repeated unbuffered DI water extraction was conducted with a lower biochar:solution ratio of 1:20, smaller biochar particle size and a surfactant (see section 2.4) to assess the time-dependent P release. In the 1<sup>st</sup> extraction step 16.6% of the total P present in RH 700 biochar was released and nearly 40% after the 6<sup>th</sup> extraction step (Table 2). This indicates that P in our rice husk biochar is initially released when extracted close to the native biochar pH (~9.5 in the first extraction step) and continues to be released until at least 40% of the total P is extracted with potential further P release. These results suggest that rice husk biochar is a suitable P fertiliser which is confirmed in other studies (e.g. Sun et al., 2018).

176 Repeated extraction decreased the EC from  $425 \pm 21 \mu\text{S cm}^{-1}$  in the initial extraction to  $78 \pm 4 \mu\text{S cm}^{-1}$   
177 after the 6<sup>th</sup> step (Table 2). At the same time, the solution pH gradually decreased, from  $9.49 \pm 0.12$  to  
178  $8.83 \pm 0.18$  (Table 2).

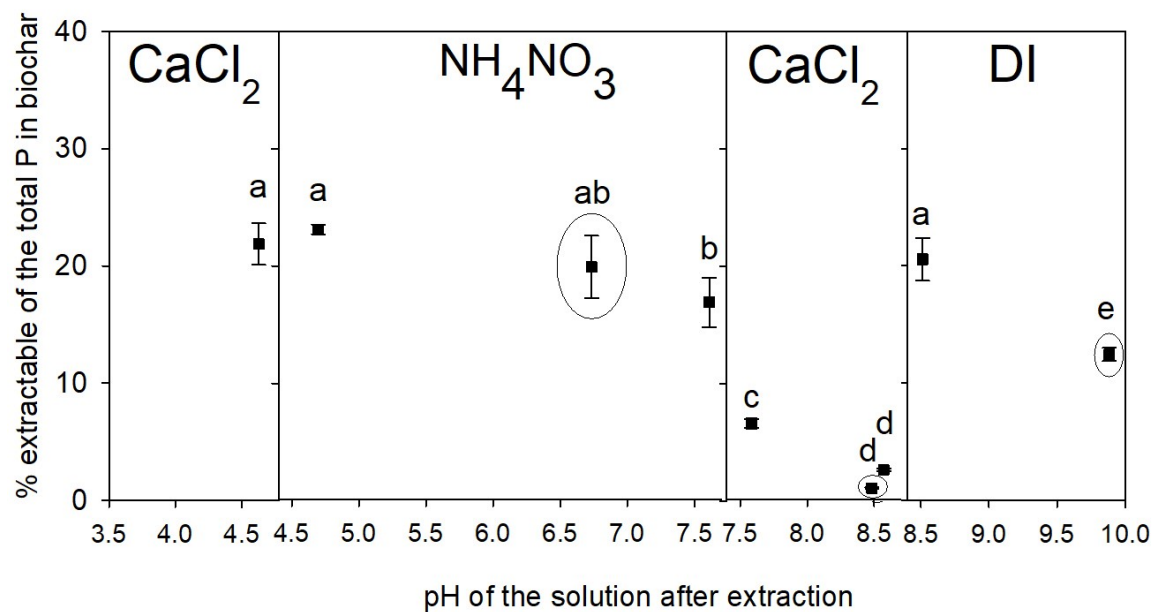


Figure 1: Proportion of total P mass in RH 700 biochar (rice husk, 700°C) extracted using three different extractants (0.01 M CaCl<sub>2</sub>, 1 M NH<sub>4</sub>NO<sub>3</sub>, deionised water (DI)) at different pH. All values are means and one standard deviation (n = 4). Unbuffered pH conditions (highlighted by the ellipses) and buffered pH conditions were used. The x-axis represents the pH values after the extraction (equal to the pH prior to extraction for buffered solutions, variable for unbuffered). Different lower-case letters indicate statistical differences determined via one-way ANOVA and Tukey post-hoc tests.

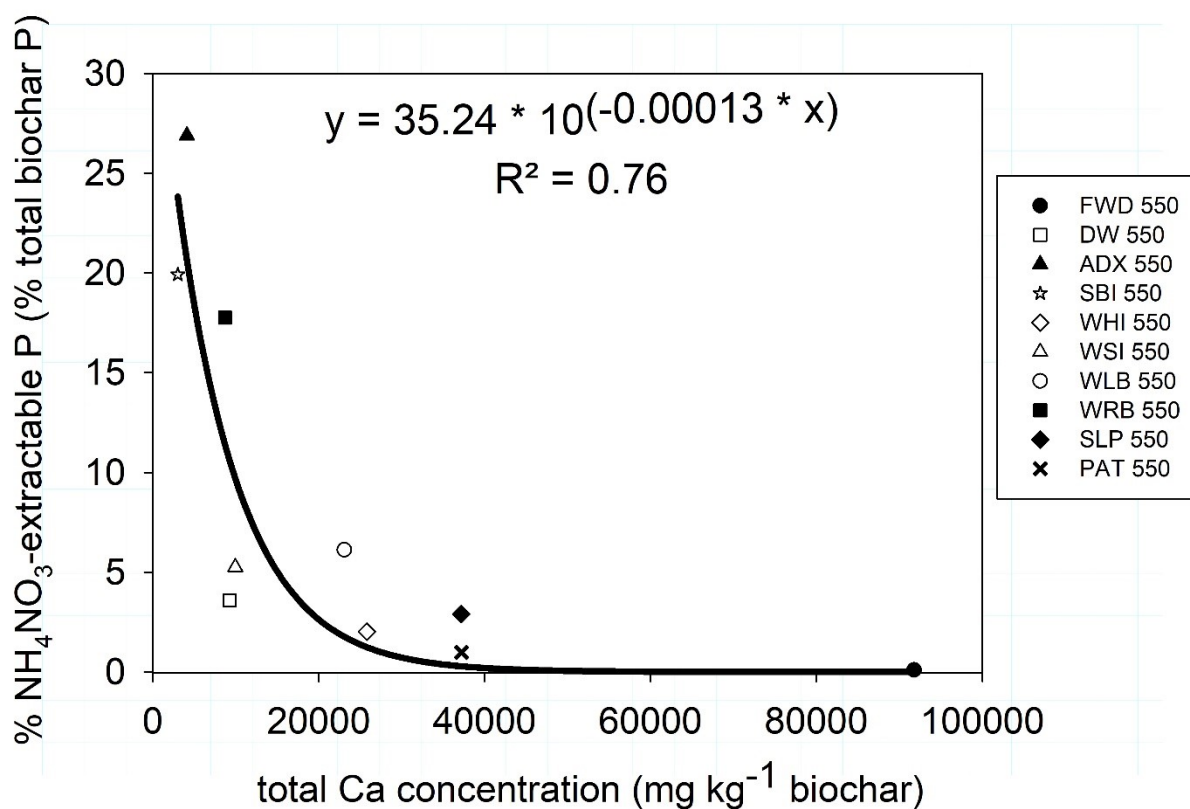


Figure 2: Relationship between % available of total P concentration in biochars determined via unbuffered 1 M  $\text{NH}_4\text{NO}_3$  extractions and biochar total Ca concentration. Ten biochars produced at  $550^\circ\text{C}$  from ten different feedstocks are shown. Data based on Buss et al. (2016a, b).  $R^2 = 0.76$ , standard error of the estimate = 4.8762, p-value determined via ANOVA = 0.001.

### 3.2 Effect of Ca on biochar P release

The proportion of total P extracted from RH 700 biochar with  $\text{CaCl}_2$  at a pH between 7.6 and 8.6 was much lower than for other extractions, resulting in P release of only 1.1% (unbuffered pH), 2.9% (buffered at pH 8.6) and 6.8% (buffered at pH 7.6) (Figure 1), whereas  $\text{CaCl}_2$  at pH 4.6 extracted 21.9% of the total P. This clearly shows that the combination of  $\text{CaCl}_2$  together with the higher pH environment limits biochar P availability. At a pH between 7.5 and 9.0, P binds to Ca and forms di- and tri-calcium phosphates (Chow, 2001; Blume et al., 2016). The low water solubility of these P forms can result in precipitation on biochar surfaces as previously described for fast pyrolysis biochars (Qian et al., 2013). At pH exceeding 9.0, di-calcium phosphates (anhydrous and dehydrate) are more soluble (Chow, 2001).

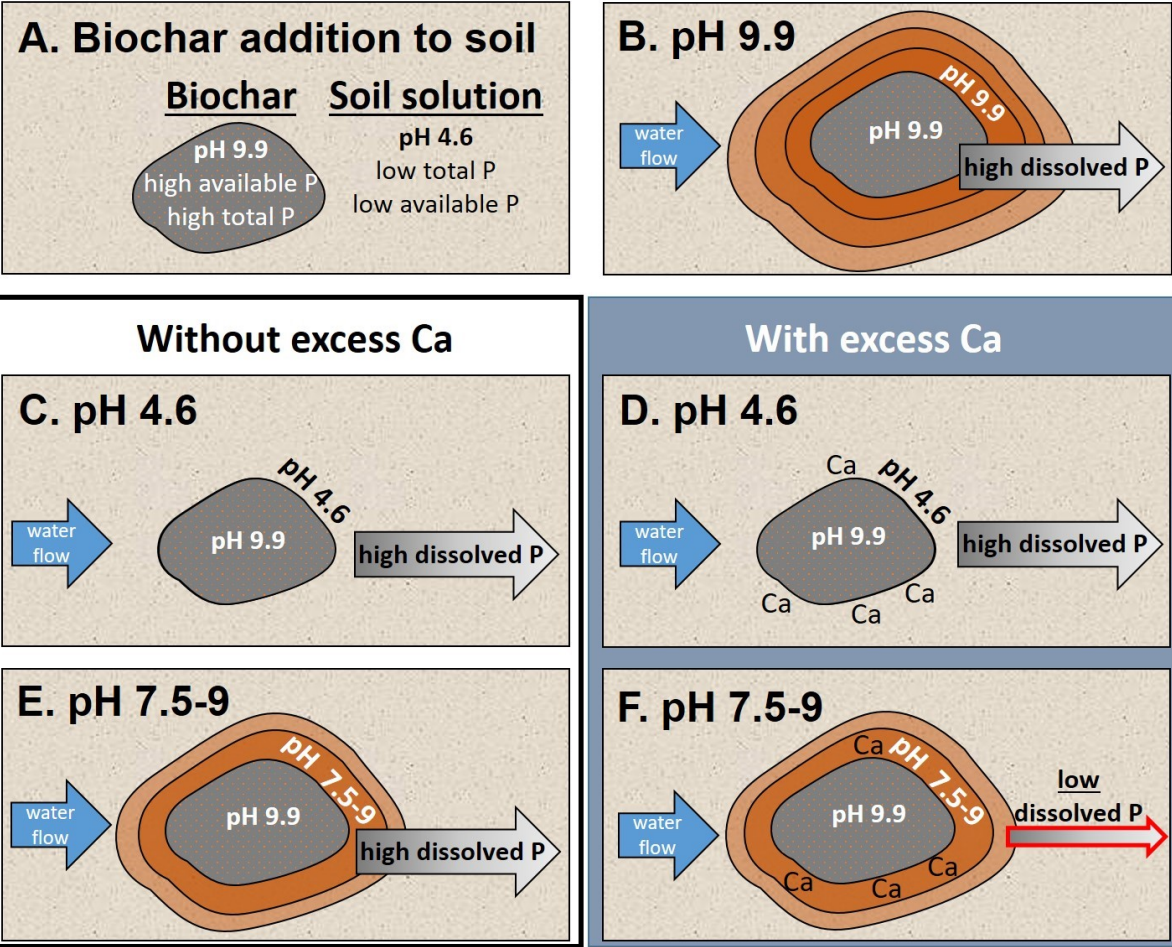
We investigated whether only external Ca immobilises P or whether internal Ca from the biochar itself can immobilise P. Analysis of previously published data for 10 biochars (produced at 550°C to exclude any effect of pyrolysis temperature) showed that higher biochar total Ca concentrations (Buss et al., 2016b) are significantly associated with decreasing 1 M  $\text{NH}_4\text{NO}_3$ -extractable P (Buss et al., 2016a) ( $R^2 = 0.76$ ,  $p = 0.001$ ; Figure 2). It is likely that calcium phosphates formed either during pyrolysis and/or after initial P release from biochar which subsequently precipitated with biochar Ca.

The RH 700 biochar has a Ca concentration of  $\sim 1700 \text{ mg kg}^{-1}$  and released 19.9% of total P when extracted under the conditions used to define the relationship above (unbuffered 1 M  $\text{NH}_4\text{NO}_3$ , final pH 6.7) which fits well with the general exponential model (Figure 2). This provides strong evidence that biochar P can be rendered unavailable through the effect of Ca supplied externally from the soil solution or from within biochar itself. Ca concentrations in biochar below 1% are recommended which is a threshold value where the concentration of available P increased drastically in our study.

213 Table 2: Quantitative and cumulative P release, solution pH and solution electrical conductivity (EC) for RH  
 214 700 (rice husk, 700°C) biochar after extraction with unbuffered DI water in six repeated extractions. Means and  
 215 one standard deviation depicted with n = 3.

extraction step	biochar P released		pH	EC
	mg kg <sup>-1</sup> mean ± SD	% of total P, cumulative	mean ± SD	μS cm <sup>-1</sup> mean ± SD
1	258 ± 2.9	16.6	9.49 ± 0.12	425 ± 20.5
2	137 ± 2.4	25.4	9.57 ± 0.05	221 ± 15.3
6	34 ± 0.8	38.9	8.83 ± 0.18	77.8 ± 4.2

216



219 Figure 3: Model for P release from alkaline biochar in an acidic, nutrient-poor soil showing different scenarios  
220 of biochar-soil interaction with and without excess Ca (originating from the soil solution or from the biochar  
221 itself). The biochar-soil interface pH is depicted in each figure in the upper left-hand corner. Panel A shows the  
222 initial state when biochar is added to soil. In B the development of a pH gradient between biochar and the soil  
223 due to ash leaching out of biochar is depicted (concentric rings) which increases the pH at the biochar-soil  
224 interface. Scenarios C and D represent a well buffered soil environment so there is no pH gradient between the  
225 biochar particle, in contrast to less buffered conditions in scenarios E and F.

### **3.3 A model for P release as affected by biochar-soil pH gradient and Ca concentration**

Our results demonstrate that P release from biochar is limited by the same factors that govern P availability in soil. The difference is, however, that when biochar is applied to soil, soil solution composition and pH are affected by both soil and biochar. Therefore, here we propose a conceptual model to delineate the P release from rice husk biochar when applied to acidic soil with different buffering capacity as affected by CEC, soil texture and mineralogy. The starting conditions after biochar addition to the soil are shown in Figure 3A.

The pH at the interface of biochar and soil is expected to be determined by the pH of the biochar resulting from migration of soluble alkaline elements from biochar ash (Figure 3B). These components lead to a pH gradient developing around the biochar particle reflecting the limited buffering capacity of strongly weathered or sandy soils. Under these conditions with pH at the soil-biochar interface similar to the biochar pH measured in water (9.9), P flows readily (12.5% of P extracted), although not as readily as at lower pH.

In a well buffered soil environment, such as a clay soil, where bulk soil pH is barely affected by biochar pH, there is no pH gradient and the pH surrounding the biochar will be governed by soil pH (Figure 3C). Our results suggest that in this scenario, biochar P will be released initially (20% of total P in our study). However, it will depend on the composition of soil and soil solution (in particular Al and Fe) whether the P continues to be released or becomes immobilised (Blume et al., 2016). Excess Ca from the soil solution or leached from the biochar in this case would not affect the P release (Figure 3D) since the solubility of calcium phosphates is high at low pH (Chow, 2001).

A scenario between these two extremes is likely in most situations, for a soil with average buffering capacity. Here a gradient of pH develops between the biochar and the soil, and the resulting pH around the biochar will be in the range 4.6–9.9. P will be readily released independent of Ca, Fe and Al in soil solution at a pH between 6.0 and 7.0 (Blume et al., 2016; Ruysschaert et al., 2016). When the pH around the biochar is in the range ~7.5–9.0 (Figure 3E), it can be assumed that P moves



readily from biochar to soil. In contrast, a high concentration of Ca around the biochar in combination with a pH of ~7.5–9.0 (Figure 3F) may lead to very low availability and delivery of P to the soil (around 1% of total P) due to the precipitation of calcium phosphates. The excess Ca needed for P precipitation can originate from the soil solution (represented in our study by the CaCl<sub>2</sub> extractions) or from the biochar itself (demonstrated by the relationship between biochar extractable P and biochar total Ca). Biochars typically display pHs of 7–11 (Qambrani et al., 2017) and it is highly likely that in biochar-amended soil the pH at the soil-biochar interface will be 7.5–9.0, leading to P precipitation. The key unknown then concerns the effect of direct interaction between plant roots and the biochar interface, and whether the biochar composition can be manipulated, in order to maximise transfer of recycled P. Characterising P-Ca speciation in biochar using XANES (e.g. Liang et al. (2017)) could facilitate further understanding of the mechanisms and controls on P release from biochar.

## 4 Conclusion

The release of P in biochar was reduced at a pH of 7.5–9.0 and when excess Ca was present. We anticipate that biochar total Ca concentration will provide a good predictor of its P availability. To increase the P delivery, low Ca concentrations (<1%) in biochar and/or a pH lower than ~7.5 are required. Conversely, higher Ca concentrations support some chemical restriction on biochar P release. Whilst based on results for one biochar only, the new conceptual model proposed here provides a framework that can be developed further to assess the potential of different biochars to provide P for crops under different soil pH and buffering conditions.

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**Supplemental material.** Supplemental material contains results of tests of DEPP buffer concentration on extractable nutrients from biochar (Supplemental Table S1).

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